

Dissipative particle dynamics with energy conservation

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Abstract

The stochastic differential equations for a model of dissipative particle dynamics with both total energy and total momentum conservation in the particle-particle interactions are presented. The corresponding Fokker-Planck equation for the evolution of the probability distribution for the system is deduced together with the corresponding fluctuation-dissipation theorems ensuring that the *ab initio* chosen equilibrium probability distribution for the relevant variables is a stationary solution. When energy conservation is included, the system can sustain temperature gradients and heat flow can be modeled.

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Much attention has recently been paid to the simulation strategy for the dynamics of complex fluids known as *Dissipative Particle Dynamics* (DPD), which was first introduced by Hoogerbrugge *et al.*[1]. In this model, a system of *mesoscopic* particles can interact via direct conservative potentials, as in molecular dynamics (MD) simulations but, in addition, the particles exert friction and brownian forces on each other. The dissipative and random interactions are chosen in such a way that the center of mass motion of each interacting pair is insensitive to their action. In this way, the system relaxes to its equilibrium much faster than in MD simulations and, at the same time, the interaction conserves the total momentum. This second feature allows the system to exhibit a hydrodynamic behaviour from a macroscopic point of view. The model is isotropic and Galilean-invariant, in contrast with models defined on a lattice, and has the potential to be computationally efficient.

Thus, DPD appears as an interesting tool although its capability for making quantitative predictions on the dynamics of complex systems remains still to be explored. Some steps forward, however, have already been taken. For instance, Español *et al.*[2] have

derived the fluctuation-dissipation theorem appropriate to these dissipative particles, the true hydrodynamic behaviour of the model has been proved[3] and the relationship of the macroscopic transport coefficients with the mesoscopic parameters defining the model has been established[4]. The DPD method has also been applied with remarkable success to account for the many-body problem of the hydrodynamic interactions in colloidal suspensions[5] as well as to domain growth in binary immiscible fluids[6].

As originally formulated, DPD can only deal with isothermal conditions since the energy is not conserved in the interaction[4]. The system therefore cannot sustain temperature gradients and, hence, no heat flow can be modeled[4]. This limitation excludes the DPD simulation strategy from those problems in which non-equilibrium situations involving temperature gradients or heat generation are important, as is the case for convection or in chemical reactions. The aim of this letter is to extend the DPD algorithm to account for both momentum and energy conservation in the particle-particle interaction, whilst maintaining the irreversible nature of these interactions.

The dissipative particles can be viewed as *lumps*[4] or *clusters* of true physical particles or as particles with internal structure bearing some degrees of freedom. The DPD model is mesoscopic in nature since it resolves only the overall center-of-mass motion of the cluster and avoids the description of the variables specifying its *internal state*. We will account for the energy stored in the internal degrees of freedom of the particles without explicit consideration of any internal Hamiltonian, in a model inspired by the treatment of hydrodynamic fluctuations[7, 8, 9].

Our model is based on the following assumptions:

1. The system contains N particles interacting with each other via conservative as well as dissipative interactions. The conservative interactions are described by the Hamiltonian

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) \equiv \sum_i^N \left\{ \frac{p_i^2}{2m} + \sum_{j>i}^N \psi(r_{ij}) + \psi^{ext}(\vec{r}_i) \right\} \quad (1)$$

where $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$. The Hamiltonian depends on the momenta and positions of all the particles. The particles interact with each other through pair potentials, $\psi(r_{ij})$, which depend only on the distance between the particles, and with an external field, $\psi^{ext}(\vec{r}_i)$.

2. In addition, the particles can store energy in some internal degrees of freedom. The internal energy, u_i with $u_i \geq 0$, is introduced as a new relevant coordinate. Together with the momentum \vec{p}_i and the position \vec{r}_i this completely specifies the state of the dissipative particle at a given instant t .
3. The particle-particle interaction is pairwise and conserves the total momentum, the total angular momentum and the total energy when the internal energy of the pair is taken into account.
4. The internal states of the particle have no dynamics in the sense that they are always in equilibrium with themselves. This allows us to define a function $s_i(u_i)$.

This function can arbitrarily be chosen according to the user's need, only constrained to the requirements: a) s_i must be a differentiable monotonously increasing function of u_i , so that the function $u_i(s_i)$ exists and $\theta_i \equiv \partial u_i / \partial s_i$ exists and is always positive, and b) $s_i(u_i)$ is a *concave* function of its argument[10]. Defined in this way, s_i can be viewed as a mesoscopic *entropy* of the i^{th} particle, and θ_i can be seen as the particle's *temperature*. The change in u_i and in s_i are related by a Gibbs equation[7] $\theta_i ds_i = du_i$, which implies $\theta_i \dot{s}_i = \dot{u}_i$, where the dot over the variables is used to denote time-differentiation from now on.

5. In the absence of random terms, the pairwise particle-particle interaction is irreversible and must satisfy $\dot{s}_i + \dot{s}_j \geq 0$, where i and j label an arbitrary pair of particles in interaction with each other.
6. u_i , s_i and θ_i must remain unchanged under a Galilean transformation, so that these variables are true scalars.
7. The equilibrium probability distribution for the relevant variables of the system under isothermal conditions is chosen to be

$$P_e(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) \sim e^{-H(\{\vec{r}_i\}, \{\vec{p}_i\})/kT} \prod_{i=1}^N e^{s_i(u_i)/k - u_i/kT} \quad (2)$$

where k is Boltzmann's constant and T is the thermodynamic temperature. The first factor on the right hand side of eq. (2) contains the probability distribution for the variables $\{\vec{r}_i\}, \{\vec{p}_i\}$ as given from equilibrium statistical mechanics. The second factor on the right hand side corresponds, in turn, to the probability distribution for the internal energy of the particles as obtained from equilibrium fluctuation theory[10]. The maximum of $s_i(u_i)/k - u_i/kT$ takes place at $\theta_i = T$, in agreement with our interpretation of θ_i as the particle's temperature. Once the equilibrium probability distribution is set, all the thermodynamic properties of the model can be derived from the partition function $Z(T, V, N) \equiv \int (\prod_i d\vec{p}_i d\vec{r}_i du_i) P_e(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\})$.

We proceed to the analysis of the dynamics of the model defined so far, although the details of the calculation will be given elsewhere. For simplicity, we will analyse two particles, i and j say, due to the pairwise additivity of the interaction, and give the complete expression at the end. Since the state of the system is specified by the set $\{\vec{r}_i\}, \{\vec{p}_i\}$ and $\{u_i\}$, we have to supply equations for the evolution of these variables. The change in the position and momentum of the i^{th} particle due to the interactions with the j^{th} particle is given by

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m} \quad (3)$$

$$\dot{\vec{p}}_i = \vec{F}_{ij}^C + \vec{F}_i^{ext} + \vec{F}_{ij}^D + \vec{F}_{ij}^R \quad (4)$$

where $\vec{F}_{ij}^C = -\partial\psi(r_{ij})/\partial\vec{r}_i$ and $\vec{F}_i^{ext} \equiv -\partial\psi^{ext}(\vec{r}_i)/\partial\vec{r}_i$ are the forces due to the conservative interactions. \vec{F}_{ij}^C is, by construction, directed along the unit vector $\hat{r}_{ij} \equiv (\vec{r}_j - \vec{r}_i)/r_{ij}$.

\vec{F}_{ij}^D stands for the dissipative particle-particle interaction force and \vec{F}_{ij}^R is the random force associated with the former. The mechanisms driving the change in the internal energy of the particles are assumed to be of two kinds. On the one hand, the work done by the dissipative forces increases the internal energy of the interacting particles. Since they are identical, we assume that this work is shared in equal amounts by the particles and is irrespective of the temperatures θ_i and θ_j . At the same time, the action of the random force *cools* the particles transferring internal energy back to mechanical energy. We want, in addition, that viscosity and thermal conductivity can be independently modeled. Hence, we also consider, on the other hand, that interacting particles can exchange internal energy if $\theta_i \neq \theta_j$, something that we can call *mesoscopic heat flow* \dot{q}_{ij}^D between particles. Associated with this dissipative current, we also add a random heat flow \dot{q}_{ij}^R . Thus, we write

$$\dot{u}_i = \frac{1}{2m}(\vec{p}_j - \vec{p}_i) \cdot (\vec{F}_{ij}^D + \vec{F}_{ij}^R) + \dot{q}_{ij}^D + \dot{q}_{ij}^R \quad (5)$$

The dissipative and random terms have to be of the form $\vec{F}_{ij}^{D,R} \sim \hat{r}_{ij}$ and $\dot{q}_{ij}^{D,R} = -\dot{q}_{ji}^{D,R}$. Otherwise, the requirements of point 3 would be violated.

The analysis of point 5, permits the identification of the so-called *thermodynamic forces*[7] causing the dissipative currents to exist. In our case, it is rather intuitive that the friction forces are due to the momentum difference between interacting particles, and that the heat flow is due to a temperature difference. We, thus, assume linear relationships of the form

$$\vec{F}_{ij}^D = \zeta(r_{ij}) \frac{1}{m} \hat{r}_{ij} \hat{r}_{ij} \cdot (\vec{p}_j - \vec{p}_i) \quad \text{and} \quad \dot{q}_{ij}^D = \lambda(r_{ij}) \left(\frac{1}{\theta_i} - \frac{1}{\theta_j} \right) \quad (6)$$

where $\zeta(r_{ij})$ and $\lambda(r_{ij})$ are arbitrary positive coefficients, that are even functions under time-reversal[11]. A convenient choice is to assume them to be functions of the slow variable r_{ij} only. Galilean invariance of \vec{F}_{ij}^D and \dot{q}_{ij}^D is thus guaranteed. In this way, all the deterministic interactions are completely specified.

The properties of the random terms are chosen to also parallel the theory of hydrodynamic fluctuations[8, 9]. Since \vec{F}_{ij}^D and \dot{q}_{ij}^D are not coupled, we will demand that the random terms \vec{F}_{ij}^R and \dot{q}_{ij}^R be statistically independent. They can be written in the form

$$\vec{F}_{ij}^R = \hat{r}_{ij} \Gamma_{ij} \mathcal{F}_{ij}(t) \quad \text{and} \quad \dot{q}_{ij}^R = \text{Sign}(i - j) \Lambda_{ij} \mathcal{Q}_{ij}(t) \quad (7)$$

where the function $\text{Sign}(i - j)$ is 1 if $i > j$ and -1 if $i < j$, ensuring that $\dot{q}_{ji}^R = -\dot{q}_{ij}^R$. The scalar random variables \mathcal{F}_{ij} and \mathcal{Q}_{ij} are stationary, Gaussian and white[12, 11], with zero mean and correlations

$$\langle \mathcal{F}_{ij}(t) \mathcal{F}_{kl}(t') \rangle = \langle \mathcal{Q}_{ij}(t) \mathcal{Q}_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \quad (8)$$

Γ_{ij} and Λ_{ij} are functions to be determined later. Note that ζ and Γ_{ij} are, respectively, $\gamma\omega_D$ and $\sigma\omega_R$ in ref.[2].

The stochastic differential equations eqs. (3), (4) and (5), together with eqs. (6) and the properties of the random terms given in eqs. (7) and (8), lead to the Fokker-Planck

equation

$$\frac{\partial}{\partial t} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) = L^{con} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) + L^{dif} P(\{\vec{r}_i\}, \{\vec{p}_i\}, \{u_i\}) \quad (9)$$

where the *convective* operator, L^{con} , and the *diffusive* operator, L^{dif} , are defined as

$$\begin{aligned} L^{con} \equiv & - \sum_{i=1}^N \left[\frac{\partial}{\partial \vec{r}_i} \cdot \frac{\vec{p}_i}{m} + \frac{\partial}{\partial \vec{p}_i} \cdot \vec{F}_i^{ext} \right] - \sum_{i,j \neq i}^N \left\{ \frac{\partial}{\partial \vec{p}_i} \cdot \left[\vec{F}_{ij}^C + \zeta(r_{ij}) \frac{1}{m} \hat{r}_{ij} \hat{r}_{ij} \cdot (\vec{p}_j - \vec{p}_i) \right] + \right. \\ & \left. + \frac{\partial}{\partial u_i} \left[\frac{1}{2m^2} \zeta(r_{ij}) [(\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij}]^2 + \lambda(r_{ij}) \left(\frac{1}{\theta_i} - \frac{1}{\theta_j} \right) \right] \right\} \end{aligned} \quad (10)$$

$$\begin{aligned} L^{dif} \equiv & \sum_{i,j \neq i}^N \left\{ \frac{\partial}{\partial \vec{p}_i} \cdot \frac{1}{2} \Gamma_{ij}^2 \hat{r}_{ij} \hat{r}_{ij} \cdot \vec{\mathcal{L}}_{ij} + \right. \\ & \left. + \frac{\partial}{\partial u_i} \left[\frac{1}{2m} (\vec{p}_j - \vec{p}_i) \cdot \frac{1}{2} \Gamma_{ij}^2 \hat{r}_{ij} \hat{r}_{ij} \cdot \vec{\mathcal{L}}_{ij} + \frac{1}{2} \Lambda_{ij}^2 \left(\frac{\partial}{\partial u_i} - \frac{\partial}{\partial u_j} \right) \right] \right\} \end{aligned} \quad (11)$$

where we have in addition defined the operator

$$\vec{\mathcal{L}}_{ij} \equiv \left(\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right) + \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \left(\frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \quad (12)$$

Imposing that the equilibrium distribution function given in eq. (2) is a stationary solution of eq. (9)¹, we derive the corresponding fluctuation-dissipation theorems

$$\Gamma_{ij}^2 = 2k \Theta_{ij} \zeta_{ij} \quad (13)$$

$$\Lambda_{ij}^2 = 2k \lambda_{ij} \quad (14)$$

where we have defined the mean inverse temperature as $\Theta_{ij}^{-1} = (1/\theta_i + 1/\theta_j)/2$, that is a function only of u_i and u_j . Eq. (9) together with eqs. (13) and (14) are a generalization of the results found in ref.[2], which refer to isothermal conditions and momentum conservation only. A crucial difference regarding the momentum change is, however, the fact that the fluctuation-dissipation theorem given in eq. (13) relates the strength of the random force with the temperature Θ_{ij} , instead of the thermodynamic temperature T [2]. Thus, the model presented here is defined in terms of particle properties only, with no reference to macroscopic magnitudes such as the thermodynamic temperature or the density of the system. This neat property permits the use of DPD in situations other than isothermal. Together with the updating algorithms shown below and the second fluctuation-dissipation, eq. (14), this is the main result of this letter.

Note that the Langevin equations eqs. (4) and (5) are subject to the so-called Itô-Stratonovich dilemma[13] due to the occurrence of products of fast variables, such as \vec{p}_i or Θ_{ij} , and random variables which are δ -correlated in time. We take, however, eq. (9) as the true definition of the random processes. The choice made here for these random processes

¹In fact, the probability flux must also vanish for a system in thermodynamic equilibrium[11]

is based on the *detailed balance condition* and on the *weak coupling assumption*[11], which permit that the properties of the random forces be independent of overall thermodynamic properties. Finally, the updating algorithms can directly be obtained from eq. (9), using eqs. (13) and (14), with no ambiguity. After some algebra, we obtain the new values of the variables $\vec{r}'_i \equiv \vec{r}_i(t + \delta t)$, $\vec{p}'_i \equiv \vec{p}_i(t + \delta t)$ and $u'_i \equiv u_i(t + \delta t)$ in terms of the old ones at t

$$\vec{r}'_i = \vec{r}_i + \frac{\vec{p}_i}{m} \delta t \quad (15)$$

$$\begin{aligned} \vec{p}'_i &= \vec{p}_i + \left\{ \vec{F}_i^{ext} + \sum_{j \neq i} \left[\vec{F}_{ij}^C + \frac{1}{m} \xi (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \hat{r}_{ij} \right] \right\} \delta t + \\ &+ \sum_{j \neq i} \hat{r}_{ij} \sqrt{2k\Theta_{ij}\zeta(r_{ij}) \delta t} \Omega_{ij}^{(p)} \end{aligned} \quad (16)$$

$$\begin{aligned} u'_i &= u_i + \sum_{j \neq i} \left\{ \frac{1}{2m^2} \xi [(\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij}]^2 + \lambda(r_{ij}) \left(\frac{1}{\theta_i} - \frac{1}{\theta_j} \right) - \frac{1}{m} k \Theta_{ij} \zeta(r_{ij}) \right\} \delta t + \\ &+ \sum_{j \neq i} \left\{ \frac{1}{2m} (\vec{p}_j - \vec{p}_i) \cdot \hat{r}_{ij} \sqrt{2k\Theta_{ij}\zeta(r_{ij}) \delta t} \Omega_{ij}^{(p)} + \sqrt{2k\lambda(r_{ij}) \delta t} \Omega_{ij}^{(q)} \right\} \end{aligned} \quad (17)$$

where we have defined an effective friction coefficient

$$\xi(r_{ij}, u_i, u_j) \equiv \zeta(r_{ij}) \left[1 + \frac{k}{2} \left(\frac{\partial}{\partial u_i} + \frac{\partial}{\partial u_j} \right) \Theta_{ij} \right]. \quad (18)$$

$\Omega_{ij}^{(p)}$ and $\Omega_{ij}^{(q)}$ are independent random numbers defined from the random variables \mathcal{F}_{ij} and \mathcal{Q}_{ij} and are Gaussian with zero mean and variance $\langle \Omega_{ij}^{(p)} \Omega_{kl}^{(p)} \rangle = \langle \Omega_{ij}^{(q)} \Omega_{kl}^{(q)} \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$.

The model presented in this letter constitutes a generalization of the DPD method. The addition of energy conservation in the particle-particle interaction in a consistent way, allows the derivation of an updating algorithm defined in terms of particle variables only. We have obtained two fluctuation-dissipation theorems which permit that the proper thermodynamic equilibrium be reached for the model under appropriate conditions. It should be mentioned that, with respect to previous treatments[2], the fluctuation-dissipation theorem for the random force derived in this work contains the local temperature Θ_{ij} instead of the thermodynamic temperature T , stressing the local nature of our model. In addition, the fluctuation-dissipation theorem for the heat flux has no counterpart in previous DPD formulations. The corresponding computer implementation of the model has already shown that the total energy is well conserved for an isolated system, although some dependency on the time step δt has been observed. Therefore, our model can sustain temperature gradients and thus heat flow can be described.

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